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STRENGTH AND STRUCTURE OF $Ga_{1-x}In_xAs$ ALLOYS

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The role of isovalent dopants in the high temperature deformation of GaAs has been studied in the temperature range 550°C to 1150°C. Additions of In, Sb, and B increase the high temperature hardness and the critical resolved shear stress for deformation at a given strain rate and result in lowering the dislocation density of as-grown liquid-encapsulated Czochralski GaAs crystals. Phosphorus, because of its minor influence on the lattice strain, provides little enhancement of the yield stress. The results are consistent with a solute hardening model where the solute atom surrounded tetrahedrally by four Ga or As atoms comprise the hardening cluster. Codoping with In and Si is less effective than the isovalent solutes, In, B, and Sb, and produces softening at high temperatures. Transmission electron microscopy provides evidence consistent with the athermal contribution to the friction stress arising from a solid solution hardening effect. Cursory studies on solid solution hardening in II-VI compounds, specifically, $Cd_{1-x}Mn_xTe$, demonstrate similar results. The role of dislocation damage in strained layer superlattices has also been modeled. In these multilayer structures, the damage resistance increases with decreasing layer

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REPORT SUMMARY

A. Technical Problem

In recent years it has been noted that small additions of indium, less than one atomic percent, to gallium arsenide grown from the melt greatly reduces the dislocation density to levels less than 10^2 cm/cm^3.[1] The mechanism by which this phenomenon occurs has been speculated to be solid solution hardening, in which indium, together with its four nearest neighbor arsenic atoms, acts as the hardening unit.[2] The basis of solid solution strengthening in GaAs by In is developed from the work of Mikkelson and Boyce.[3] They studied bond lengths in the Ga-In-As system by EXAFS and showed that the overall lattice parameter increases linearly with In concentration in accordance with Vegard's law. However, the Ga-As and In-As bond length remains roughly constant with In concentration. This indicates that each indium atom, together with its four nearest neighbor As atoms, acts as a center of strain analogous to a solute atom in a metal. Calculations based upon bond length changes suggest that the $InAs_4$ unit produces a local dilatation of 21%, considered to be a moderately strong solution hardener by metallic standards.

To test the hypothesis of this strengthening mechanism, a program was undertaken to examine the strength of $Ga_{1-x}In_xAs$ alloys as a function of composition and temperature. Because In would not expected to be the sole candidate for solid solution strengthening in the GaAs system, other isovalent dopants were also considered, including Sb, B, P, and the anisovalent Si. In addition to work on the III-V systems, it was also of interest to

pursue similar studies on the II-VI compounds which potentially demonstrate solid solution strengthening by isoelectronic dopants. Here, $Cd_{1-x}Mn_xTe$ was studied. The role of dislocations in strained-layer superlattices has also been examined. Specifically, damage to such structures by dislocations has been modeled.

B. General Methodology

III-V Compounds

In the first year of the study, Vickers hardness measurements as a function of temperature were used as a preliminary assessment of the solid solution strengthening, since microhardness scales with yield strength in many metallurgical systems. It was expected that microhardness would provide a good "first cut" to examine if these materials exhibit a plateau stress associated with solid solution hardening. These experiments required the design and construction of a hot hardness tester. [Appendix A]

The second year and second phase of the work consisted of uniaxial compression tests. Though more difficult to conduct than hardness tests, compression tests superseded the problem of surface degradation which occurred in hardness tests at elevated temperatures, and allowed determination of the critical resolved shear stress (CRSS) directly from the stress-strain curve. Compression tests were carried out at temperatures of 500, 700, 900, 1000, 1100, and 1150^{o}C at a strain rate of 1×10^{-4} s^{-1} in UHP argon. For tests at temperatures of 700^{o}C and above, the compression sample was immersed in B_2O_3 to prevent the

Table I. Materials Investigated

Material	Dopant Concentration (atoms/cm^3)	Dislocation Density (cm/cm^3)	Source
A. Undoped (low B)	B = $1x10^{16}$	$<3x10^3$	AT&T Engineering Research Center
B. P-doped	P = $2x10^{19}$	$5x10^4$	W. Mitchel AFWAL
C. In-doped (high B)	In = $1-2x10^{20}$ B = $5x10^{17}$	$0-10^2$	Westinghouse R&D Center
D. Sb-doped	Sb = $2x10^{19}$	$0-10^5$	W. Mitchel AFWAL
E. Undoped (high B)	B= $1x10^{17}$	10^4-10^5	Westinghouse R&D Center
F. In,Si-codoped	In = $1x10^{20}$ Si = $1x10^{18}$	$1.1x10^4$	W. Mitchel AFWAL

volatilization of As. The compositions studied are described in Table I. Materials were tested in the [001] orientation favoring the operation of multiple slip systems, and in the [123] orientation favoring a single slip system. To better understand the deformation mechanisms, yield strengths were measured as a function of strain rate (1×10^{-5} to 1×10^{-3} sec^{-1}) in the undoped crystal.

Dislocation structures of undeformed GaAs alloys and specimens deformed to various levels of strain were characterized by transmission electron microscopy. TEM observations were made by cutting thin slices of GaAs in the desired orientation, followed by mechanical polishing and ion milling. These

specimens were examined in a JEOL JEM 200CX transmission electron microscope at 200 keV using a double tilt goniometer stage. Characterization of the dislocation structures has been performed by the standard g·b criterion. Electron microscopy results together with the deformation data have been used to elucidate the strengthening mechanism.

II-VI Compounds

In the II-VI system, compositions across the CdTe-MnTe binary phase diagram were obtained from Professor Jack Furdyna of the University of Notre Dame. The lattice misfit associated with a $MnTe_4$ tetrahedral cluster in a CdTe lattice is approximately 10% and, therefore, the presence of Mn in the lattice would be expected to strongly influence the mechanical strength. By virtue of the limited amount of material available, no uniaxial compression tests were performed. Hardness measurements of the $Cd_{1-x}Mn_xTe$ ($0<x<0.6$) crystals were made at 100^{o} increments to $500^{o}C$ on the (110) cleavage planes.

Strained Layer Superlattices

Strained layer superlattices, structures made of alternating layers of different crystals, exhibit interesting electronic properties because of the large coherency strains and the resulting reduced symmetry of the crystals. However, such structures are easily damaged by dislocations or cracks in the presence of thermally- or mechanically induced stresses. Calculations were performed to examine the resistance of strained layer superlattices to damage by dislocation injection.

C. Technical Results

Hardness Tests

Results of hardness tests are shown in Figure 1 and are described in greater detail in Appendix B. The hardness, H, is related to the critical resolved shear stress by the following relationship:

$$\sigma_{CRSS} = 0.5\ (H/3)$$

where 0.5 is an upper bound estimate of the Schmid factor which incorporates the vectors for transforming coordinate systems between the tensile axis and the slip plane. The calculated values are shown in Figure 2. Also on this graph is a comparison with undoped Bridgman crystals studied by Swaminathan and Copley [4] and undoped and In-doped crystals by Tabache et al.[5] from lower yield strength measurements. The discrepancy between the data sets was addressed in later stages of the work. Extrapolation of our data to the melting point of GaAs allows comparison with the calculated thermal stresses developed during the LEC growth process.[6] Note that the results suggest that crystals highly doped with In have sufficient solid solution hardening to prevent yielding and the accompanying dislocation generation.

Compression Tests

Materials which have been examined in this study were listed earlier in Table I. The results of uniaxial compression tests of undoped GaAs, GaAs containing B, and GaAs containing (In,B) are summarized in Figure 3. Our results show that the CRSS values more than double with In additions of $1\text{-}2\text{x}10^{20}$ atoms/cm^3. Also,

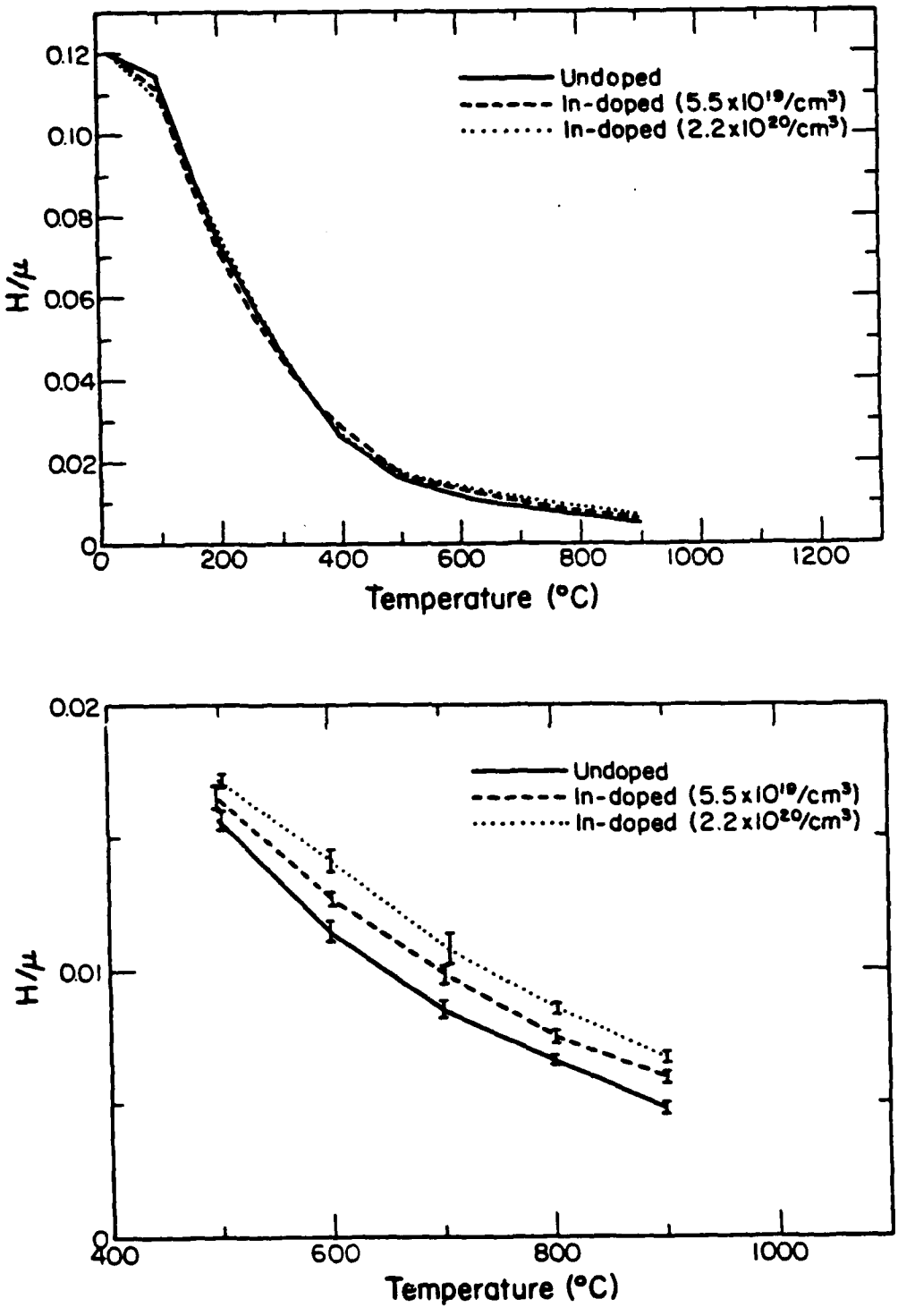

Figure 1. Normalized hardness versus temperature for GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{As}$.

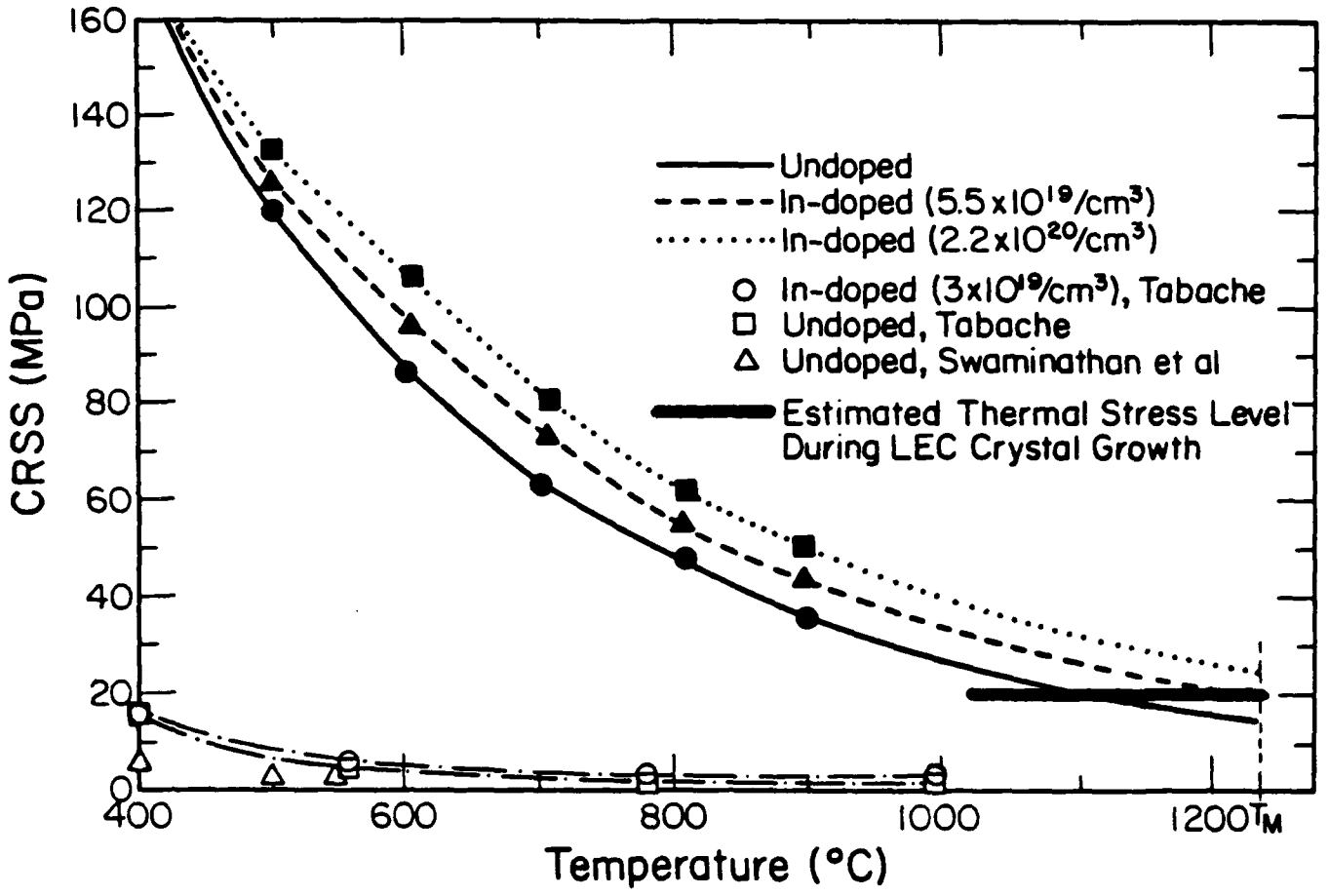

Figure 2. Critical resolved shear stress estimated from hardness data compared with compression data of Swaminathan and Copley [4] and Tabache et al. [5] on undoped and In-doped LEC GaAs.

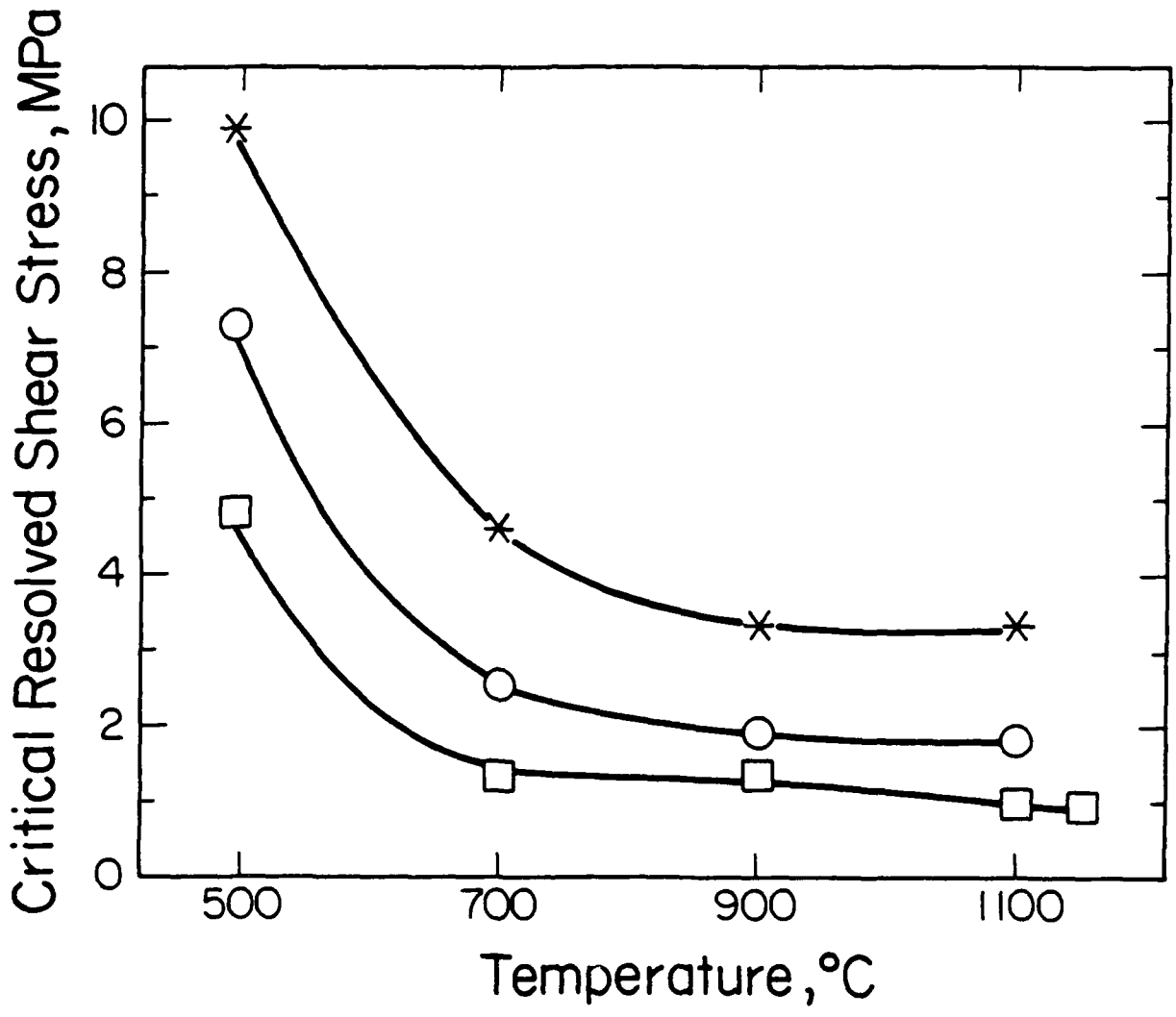

Figure 3. Variation of critical resolved shear stress (CRSS) as a function of temperature at a strain rate of 10^{-4} s^{-1} for undoped crystal A (open squares), boron-containing crystal E (open circles) and (In,B)-containing crystal C (asterisk).

the CRSS values of both the undoped and B- and (In,B)-containing crystals show a weak temperature dependence, consistent with a solid solution strengthening model. Results of Material E is consistent with the findings of Swaminathan and Copley [5], and Tabache et al.[6] suggesting that boron, which diffuses into the crystal from B_2O_3 during LEC growth, has a substantial strengthening effect. Since boron is not purposely added to the crystals, its effect is often neglected.

From the stress-strain curves of Figure 4 of Materials A and C, the onset of dynamic recovery in In-doped GaAs occurs at higher stress and strain levels suggesting that climb is more difficult in In-doped alloys compared to the undoped alloy. The strengthening observed appears to be sufficient to prevent macroscopic yield during the growth of large diameter GaAs on the basis of current models of crystal growth. Yield strength measurements as a function of strain rate provide greater evidence for the specific deformation mechanisms.(Figure 5) The strong temperature and strain rate dependences of the yield strength are observed at 500 to 700^{o}C, consistent with a small activation energy and double-kink motion with the solutes retarding the motion of the kinks. At higher temperatures, the yield strength shows a weak temperature and strain rate dependence in accordance with a larger activation energy and the pinning of dislocations. Details of these results and their interpretation are reported in Appendices C and D.

Although primary studies were performed on Materials A, C, and E (undoped and In-doped with high and low boron contents,

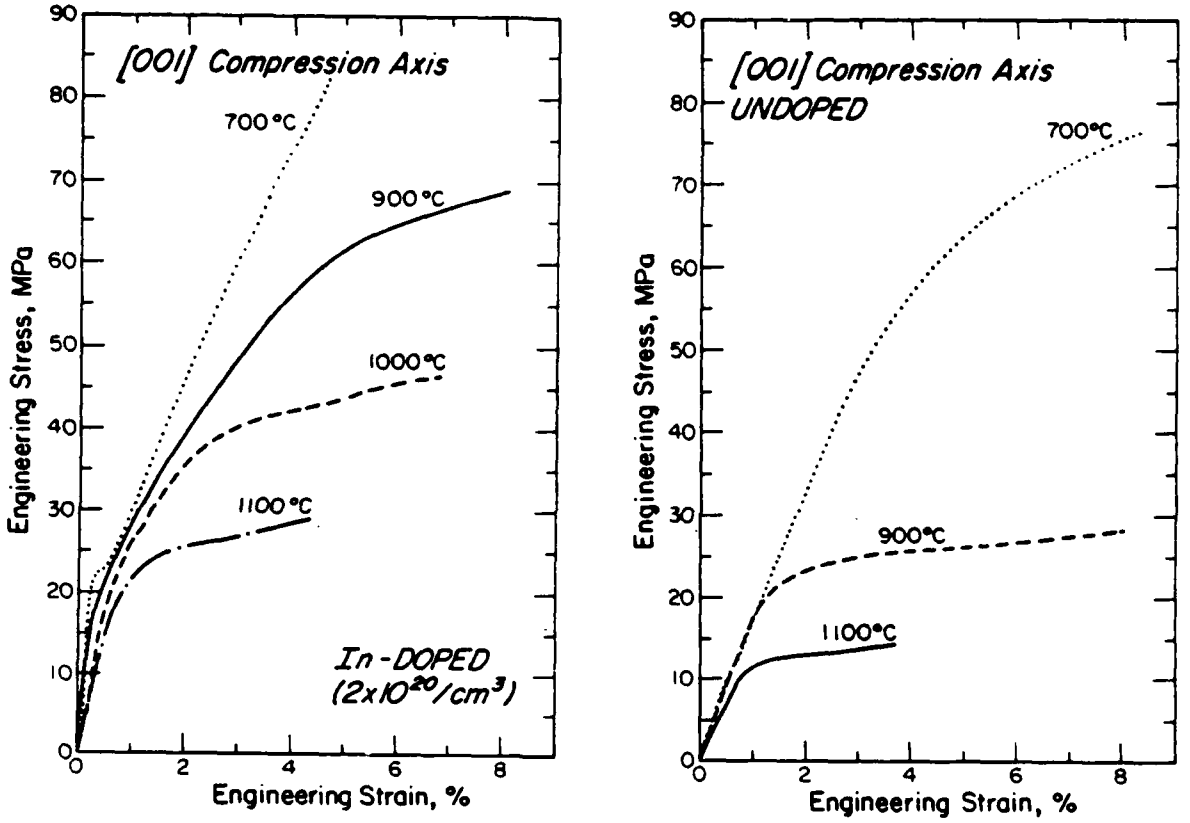

Figure 4. Engineering stress-strain curves at different temperatures for (a) In-doped GaAs and (b) undoped GaAs specimens tested in the [001] orientation.

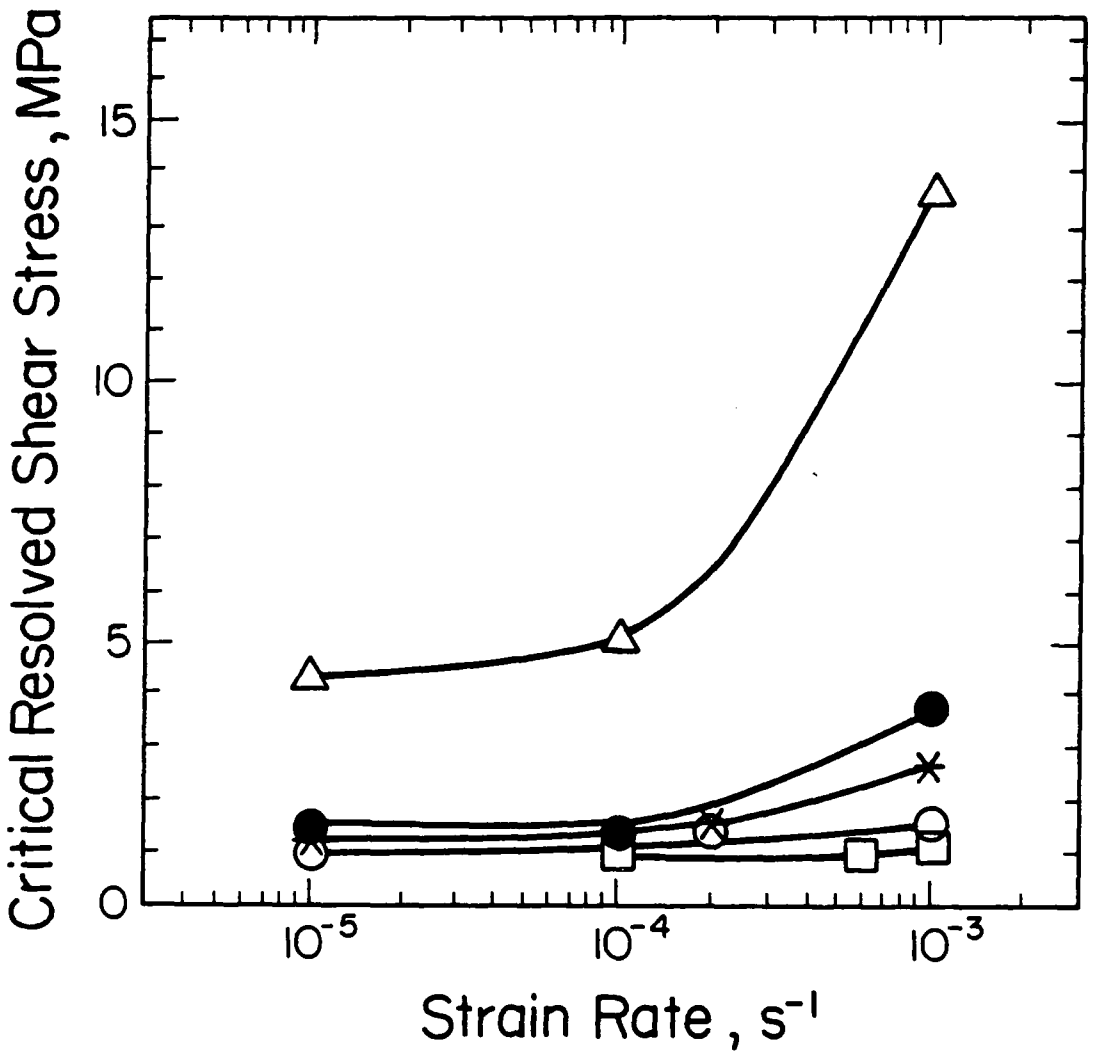

Figure 5. Variation of CRSS with strain rate for undoped GaAs (crystal A) at different temperatures. Open triangle: 500°C; solid circles: 700°C; asterisk: 900°C; open circles: 1100°C; open squares: 1150°C.

respectively), the role of other isoelectronic dopants, Sb and P, and the anisovalent Si, have been examined as well.(Table II) The solute hardening analysis indicates that the CRSS should scale with the size of the appropriate tetrahedral cluster. The pinning force of the size effect is proportional to the relative volume change, dv/v, associated with the hypothetical insertion of a solute tetrahedron into the matrix. (The volume change is related to the difference in lattice parameters of GaAs and the appropriate solute-arsenide.) Values for the calculated dv/v are listed in Table III for the isovalent dopants studied. The qualitative trends in the data are expected with the change in flow stress with change in dopant concentration monotonically increasing with dv/v. Consistent with the experimental data are dislocation densities of the as-grown crystals listed in Table I. In, (In,B) and Sb result in low dislocation densities, while P, which is expected to be a weak strengthener on the basis of our present work, is less effective at reducing dislocation densities.

Codoping with (In,Si) hardens GaAs at intermediate temperatures (500^{o}C), but appears to lower the yield strength at high temperatures. [Appendix D] Potential explanations for this behavior are many. Silicon is known to act as a donor or acceptor in GaAs. Should the distribution between these two sites change with temperature [7,8], one might expect the strengthening effect to also change with temperature. Moreover, the electrical interaction of Si with dislocations or point defects are expected to be important, but are not understood at temperatures near the melting point of GaAs. A third possible

Table II. Yield stress (critical resolved shear stress) values at a strain rate of 10^{-4} s^{-1} at different temperatures for the different materials investigated.

	CRSS (MPa)				
	500°C	700°C	900°C	1100°C	1150°C
A. Undoped (Low B)	5.10	1.33	1.45	1.00	0.96
B. P-doped	6.60	2.39	1.26	0.91	
C. In-doped	9.90	4.64	3.33	3.27	
D. Sb-doped	10.25	2.45	1.49	1.25	
E. Undoped (high B)	7.30	2.55	1.91	1.83	
F. (In,Si) Co-doped	9.37	2.04	1.26	1.28	

Table III. The change in yield stress (critical resolved shear stress) produced by doping and the size effect $\delta v/v$.

Specimen	$\lvert\delta a/a\rvert$	$\lvert\delta v/v\rvert$	$\Delta\sigma/\Delta c$ (MPa/atom%)		A [MPa/(atom%)$^{1/2}$]	
			500°C	1100°C	500°C	1100°C
A. undoped	0	0	0	0	0	0
B. p	3.6	12	641		136	-
C. In	7.2	23	796	502	535	337
D. Sb	7.8	25.4	8,710	553	1852	118
E. B	15.5	40	44,200	36,700	2102	371
F. (In,Si) Codoped			676	62	-	-

reason is that solute depletion could occur during deformation which might result in a decrease in yield strength. We have, in fact, observed plate-like precipitates in the (In,Si) crystal.

Transmission Electron Microscopy

Dislocation structures in In-doped GaAs (Material C) and undoped GaAs (Material E) deformed at 700 to 1100°C have been studied in detail. Below 700°C, the temperature dependence of the flow stress and the observation of straight screw and 60° mixed dislocations are consistent with the rate-controlling mechanism of double kink nucleation and growth. At and above 700°C, the indications are that the rate-controlling mechanism becomes the drag of jogs on screw dislocations. In support of this hypothesis, the dislocated structures at yield normally consist of straight screw dislocations.(Figure 6) This model would consistently lead to a nominally temperature independent flow stress in the plateau region for undoped crystals, a correlation that would be difficult to account for with other possible mechanisms. The solid solution hardening effect of In would provide an athermal increment of the friction stress, but still produce plateau behavior, consistent with the results presented in the previous section. Details of the electron microscopy are shown in Appendix E, F, and G.

Stacking fault energies were calculated from the separation of partial dislocations. The result indicated that the stacking fault energy was approximately 44 mJ/m^2 independent of In-doping or deformation temperature.

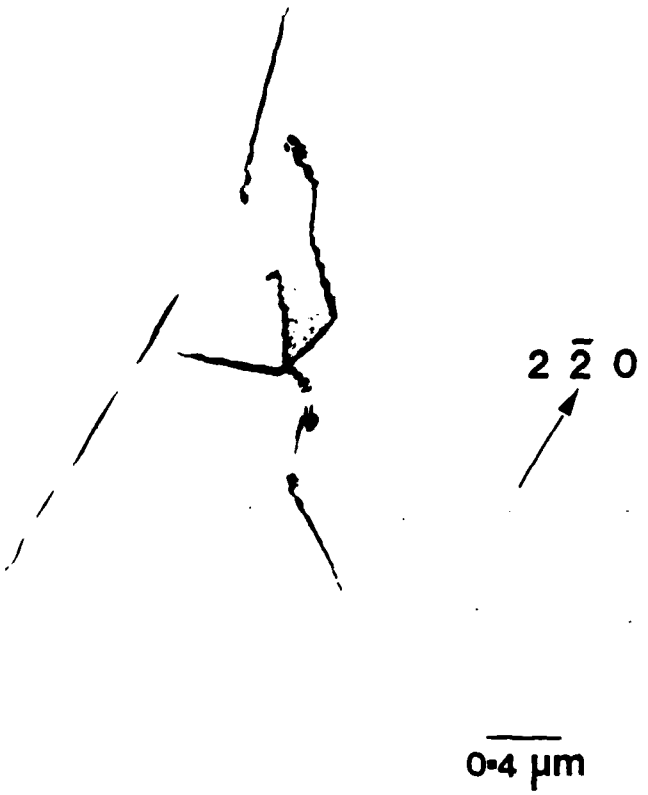

Figure 6. Electron micrograph from an In-doped specimen deformed at 700°C into the multiple slip orientation [100] in the microyield stage A to a stress of 11 MPa. Foil orientation is [111], g=[220]. Small cusps on the screw dislocations indicate local pinning of dislocations.

High Temperature Hardness of II-VI Compounds

Results on the hardness of five compositions of $Cd_{1-x}Mn_xTe$ are shown in Figure 7. Each of the $Cd_{1-x}Mn_xTe$ alloys demonstrated higher hardness than the pure CdTe across the entire temperature range. Such observations are consistent with the solute hardening model. Of the five compositions, $Cd_{0.91}Mn_{0.09}Te$ showed extensive twinning via optical microscopy and the measured hardness may not be representative of the single crystal. Larger samples for uniaxial compression are required for detailed studies on the effect of Mn on the deformation behavior of CdTe.

Damage of Strained Layer Superlattices by Dislocations

Using an approach which considered the total forces on the multilayer, i.e. the coherency and the applied stresses, the critical thickness above which dislocation generation becomes feasible has been calculated to be:

$$h_c^+ = h_c[1-\sqrt{6}(\tau/c\epsilon_o]$$

where h_c is the critical thickness in the absence of an applied stress, τ is the applied shear stress, c is the elastic constant, and ϵ_o is the misfit strain. Likewise, dislocation nucleation at the lateral surface occurs when the stress exceeds $(S^2/40\ b_I\ kT)[1-h/h^*]$ where S is the effective line tension, b_I is the Burgers vector of an interface dislocation, and h* is a function of the effective line tension, the elastic constants, and the misfit strain. As is clear from both calculations, the vulnerability to dislocation injection increases with misfit strain, layer thickness or applied stress. Details of these calculations are shown in Appendix H.

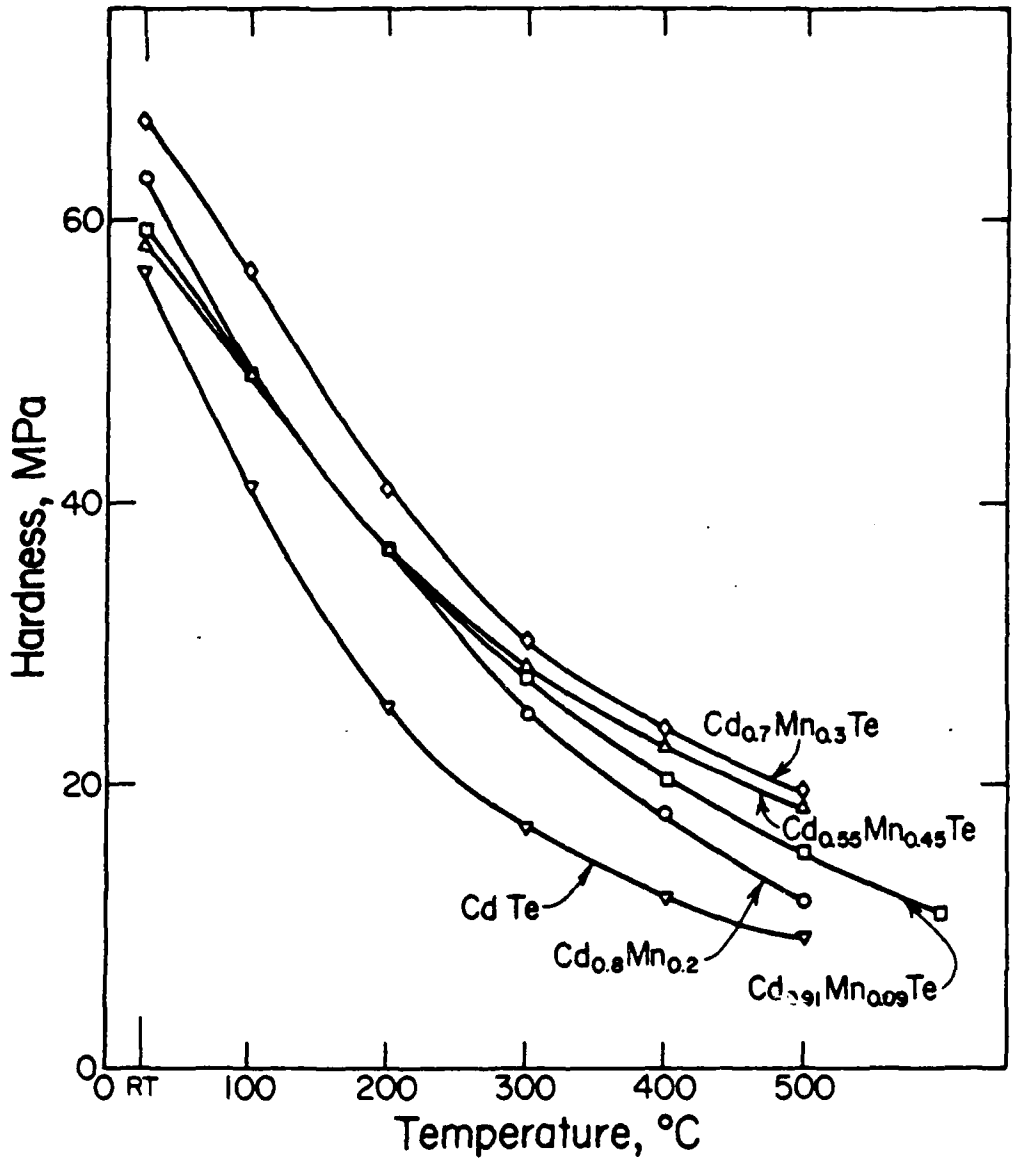

Figure 7. Vickers hardness versus temperature for $Cd_{1-x}Mn_xTe$ for $0<x<0.6$.

D. Implications

The mechanical and microscopic results of our studies suggest that the isovalent solutes In, Sb, and B cause increases in the yield strength of GaAs consistent with their role in lowering the dislocation density in as-grown GaAs crystals. The results for these solutes, and P, which is a weak hardener, are consonant with a solute hardening model for the strengthening effect. A major impediment to dislocation generation is the nucleation process, which, together with dislocation multiplication would be influenced by the solute hardening effect. These processes are expected to operate in other systems, such as the II-VI compounds, which are particularly sensitive to dislocation generation, and the group IV elements, though little experimental data have been collected to this purpose. Further studies are warranted in this area.

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1. "Mechanical Properties of $Ga_{1-x}In_xAs$", S. Guruswamy, J. P. Hirth, and K. T. Faber, Materials Research Proceedings, **56**, 329 (1986).

2. "Damage of Coherent Multilayer Structures by Injection of Dislocations or Cracks", J. P. Hirth and A. G. Evans, J. Appl. Phys., 60 [7] 2372-76 (1986).

3. "High Temperature Hardness of $Ga_{1-x}In_xAs$", S. Guruswamy, J. P. Hirth, and K. T. Faber, J. Appl. Phys., 60 [12] 4136-40 (1986).

4. "Deformation Behavior of Undoped and In-Doped GaAs in the Temperature Range 700°C to 1100°C", S. Guruswamy, R. S. Rai, K. T. Faber, and J. P. Hirth, J. Appl. Phys., 62 [10] 4130-34 (1987).

5. "Transmission Electron Microscopy Studies in $Ga_{1-x}In_xAs$", R. S. Rai, K. T. Faber, S. Guruswamy, and J. P. Hirth, pp.320-21 in Proc. 45th Ann. Meeting EMSA. Ed. by G. W. Bailey, San Francisco Press, Inc. San Francisco, CA, 1987.

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